RP186

# PHOTO-IONIZATION OF CÆSIUM BY LINE ABSORPTION

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## ABSTRACT

*Method.*—The ionization of cæsium by line absorption has been investigated by means of the space-charge method. Light resolved by a monochromator is used and the relative sensitivity in the region of line absorption, as compared to the region of continuous absorption beyond the limit, is measured.

*Ionization by a continuous spectrum.*—The effect is directly proportional to the light intensity. Relative sensitivity is independent of electrical conditions and temperature of the vapor. The reduction of the effect by an absorbing column of cæsium vapor in the light path indicates that the effective absorption line width is about 0.007 A at 0.003 mm pressure. This width increases with pressure. Relative sensitivity rises rapidly with vapor pressure between 0.0002 and 0.004 mm and drops slowly above 0.01 mm.

*Ionization by monochromatic light.*—A helium line at 3888 A is coincident with one of the cæsium lines and measurements of the absorption of this line by cæsium and of the photo-ionization produced give the probablity of ionization of an excited atom in the 4 $P_1$ state as a function of the vapor pressure.

*Discussion.*—Measurements of relative sensitivity to continuous spectrum excitation are corrected for absorption and slit width to give the probability of ionization of excited atoms in states 4 to 8 $P$ and higher states near 9 $P$, 12 $P$, 16 $P$, and 25 $P$. This probability is shown to be proportional to the chance that an excited atom collides with another cæsium atom during the life of the excited state. The probability of ionization at a collision varies from nearly one for higher states to 0.003 for the 4 $P$ state. Results are consistent with a theory of Franck's that ionization results from the combination of excited and normal atoms to form molecule ions.

## CONTENTS

# I. INTRODUCTION

## 1. THE PROBLEM

Experiments on the photo-ionization of cæsium vapor by Mohler, Foote, and Chenault [1] have shown that in addition to the predicted ionization beyond the absorption series limit resulting from continuous absorption there was some ionization by line absorption. Illumination with light from an incandescent lamp analyzed by a monochromator showed separate sharp peaks in the ionization at the fourth, fifth, sixth, and seventh lines of the principal series, while the partially or completely unresolved higher lines gave an effect which increased to a maximum at the limit (3,184 A). The third line gave a barely measurable effect and the second line no effect. Recent results by Lawrence and Edlefsen [2] show a similar phenomenon in rubidium vapor with peaks at the fourth, fifth, and sixth lines, though one other peak at 3,490 A does not coincide with an absorption line. These measurements have been made by observing the neutralizing effect of the ions on a thermionic current limited by electron space charge. The method is extremely sensitive and unaffected by surface photo-electric emission though it does not give an absolute measure of the ion current.

Mohler, Foote, and Chenault proposed the theory that the excited atoms produced by line absorption were ionized by atomic collisions in which the ionization energy (maximum 0.7 volt) came from thermal agitation. It has been pointed out in criticism [3 4] that the probability of such thermal ionization is too small to account for the observed effect, and Franck and Jordan have suggested that electron collisions with excited atoms might explain the ionization, since measurements were made in the presence of an electron current. Another suggestion of Franck's is that the excited atoms on collision with normal atoms form molecule ions.

The criticism that the ionization by line absorption is too great to be explained by thermal agitation is borne out by the following experiments, but a quantitative estimate of the probability of ionization involves a knowledge of the ratio of the number of ions produced to the number of quanta absorbed in a fine line of unknown width. For this reason Mohler, Foote, and Chenault limited their discussion to the relative heights of the peaks at the separate lines. Recent investigations of the absorption spectrum of cæsium and of the absolute value of the photo-ionization beyond the series limit offer a basis for further investigation of the ionization by line absorption.

## 2. CÆSIUM ABSORPTION

A recent paper by Waibel [5] gives quantitative measurements of the absorption by the higher series lines of cæsium. The significant datum in line absorption is the integral of the absorption coefficient across the line and to make the magnitudes measurable he used thin layers of vapor at high pressure so that lines were much broadened. The third column of Table 1 gives Waibel's observed values of $\int k d\nu$ in terms of atomic absorption coefficient and cm$^{-1}$ for the doublet

[1] Mohler, Foote, and Chenault, Phys. Rev., **27**, p. 37; 1926.
[2] Lawrence and Edlefsen, Phys. Rev., **34**, p. 233; 1929.
[3] Franck and Jordan, Anregung von Quanten Sprüngen durch Stosse, p. 126, Julius Springer, Berlin.
[4] Gudden, Lichtelektrische Erscheinungen, p. 224, Julius Springer, Berlin.
[5] Waibel, Zeits. f. Phys., **53**, p. 459; 1929.

$1S-mP_{1,2}$. The fourth column gives this integral divided by the mean frequency interval between lines $\Delta\nu=(\nu_{m+1}-\nu_{m-1})/2$. This constant ratio should equal the atomic absorption coefficient at the series limit, $k_o$. The authors [6] have published absolute measurements of the ionization produced by continuous absorption in cæsium vapor from which they compute a value of $k_o=2.3\times10^{-19}$. This is not in satisfactory agreement with the value from Waibel's data, and other measurements give still higher values. For present purposes it has seemed best to use our value of $k_o$, together with values of $\int kd\nu$ obtained by multiplying Waibel's values by 2.3/0.48 as given in column 5 of Table 1. It will be shown later that the lower value of Waibel would lead to serious inconsistencies in the present results.

TABLE 1.—*Line absorption in cæsium*

| $m$ | $1S-mP_2$ in $A$ | $\int kd\nu$ observed | $\frac{\int kd\nu}{\Delta\nu}$ | $\int kd\nu$ $k_o=2.3\times10^{-19}$ | Transmission of 4 cm at 0.01 mm |
|---|---|---|---|---|---|
| 4 | 3877 | ---- | ---- | $(550\times10^{-18})$ | 0.012 |
| 5 | 3612 | ---- | ---- | (288) | .100 |
| 6 | 3477 | $35\times10^{-18}$ | $0.40\times10^{-19}$ | 170 | .26 |
| 7 | 3398 | 20.6 | .37 | 100 | .45 |
| 8 | 3349 | 16.2 | .43 | 79 | .53 |
| 9 | 3313 | 12.7 | .48 | 62 | .61 |
| 10 | 3288 | 9.2 | .47 | 45 | .70 |
| 11 | 3270 | 7.3 | .49 | 35 | .76 |
| 12 | 3257 | 5.6 | .49 | 27 | .80 |
| 13 | 3246 | 4.3 | .47 | 21 | .84 |
| 14 | 3247 | 3.4 | .47 | 16 | .88 |
| 15 | 3231 | 2.7 | .45 | 13 | .90 |
| 16 | 3225 | ---- | ---- | (11) | .91 |

Waibel's paper includes values for the width of the lines at various pressures. Results are expressed in terms of the "half width" here denoted by $\delta\lambda$ or $\delta\nu$ which is the interval between points where $k$ has half the maximum value. The different lines of the series have nearly the same half width which varies as the square root of the pressure. For $1S-mP_2$ $\delta\lambda$ varied from 0.55 $A$ at 12.3 mm pressure to 0.30 $A$ at 4.4 mm. From this rate of variation one computes values of 0.05 $A$ at 0.1 mm, 0.015 $A$ at 0.01 mm, and 0.005 $A$ at 0.001 mm. (Pressures reduced to 0° C.) But the Doppler width for cæsium atoms at 500° K. is 0.0055 $A$ so that below 0.001 mm the Doppler broadening will be predominant. Since the lines are doublets in which each component has a hyperfine structure it becomes very complicated to compute the line shapes or widths to be expected at low pressure.

If lines have the shape theoretically predicted for collision broadening [7] then

$$\int kd\nu=k(\text{max.})\ \delta\nu \tag{1}$$

The transmission of a layer of vapor of length $L$ containing $N$ atoms per cm³ for light coincident with an absorption line is then

$$\text{trans.}=e^{-NL\int kd\nu/\delta\nu} \tag{2}$$

[6] Mohler and Boeckner, B. S. Jour. Research, **3**, p. 303; 1929.
[7] Handbuch der Physik., **20**, p. 496.

## II. EXPERIMENTAL PROCEDURE

### 1. METHOD

Figure 1 illustrates the type of space-charge tube used in most of this work. This is a quartz tube containing a platinum cylinder anode 4 cm long and 3 cm in diameter. In the ends of the anode are slits about 8 mm wide to admit light and for the cathode leads. The cathode is a hairpin platinum wire coated with oxides. The tube was usually sealed off from the pumps and heated by two independent heating units, one around the body of the tube and one around the appendix so that effects of vapor pressure and temperature could be studied independently. The ionization chamber was kept at about 500° K. for most work.

Vapor pressure was computed from an equation based on data by Kroner.[8]

$$\log p \text{ (mm)} = -3966/T + 7.1650$$

The tube was commonly operated with the filament at a barely visible red heat and with an applied voltage between zero and 1 volt which gives a dark current of the order of $2 \times 10^{-5}$ amperes. This was balanced by a bridge circuit so that current changes of $10^{-8}$ amperes

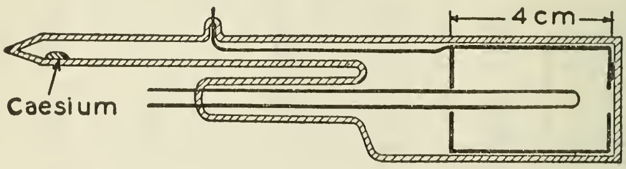


FIGURE 1.—*The type of space charge tube used in this work*

could be measured. The electron current change is of the order of $10^5$ or $10^4$ times the ion current, the ratio being greatest at low pressure.

Since the sensitivity varies with nearly all operating conditions all the observations consisted of measurements of relative sensitivity for light of frequency $\nu$ compared to light of a standard frequency in the region of continuous absorption. For experimental purposes the standard 3,150 A was chosen, though in interpreting results it is more convenient to take the series limit 3,184 A and we have reduced all results to the latter. In the following the relative sensitivity is

$$R\ (\nu) = \frac{i\ (\nu)}{i\ (3{,}184)}\ \frac{J\ (3{,}184)}{J\ (\nu)\ \Delta\nu}\ \Delta\nu\ (3{,}184) \tag{3}$$

where $i$'s are the observed current change proportional to the ionization, while the $J$'s are radiation flux in quanta per second and $\Delta\nu$ is the width of the band transmitted by the monochromator. We can safely assume that beyond the series limit the number of ions produced is equal to the number of quanta absorbed.

$$i\ (3{,}184) = cNLk_o\ J\ (3{,}184)\ \Delta\nu\ (3{,}184)$$

[8] Rowe, Phil. Mag., **3**, p. 534; 1927.

where $N$ is the number of atoms per cm$^3$ ($2 \times 10^{16}$ at 1 mm), $L$ is the path length, and $k_o$ is the atomic absorption coefficient. The proportionality factor $c$ between ions and current change is always eliminated by taking ratios.

## 2. RADIATION FLUX

The source of continous radiation was the light from a 400-watt Mazda projection lamp analyzed by a Bausch & Lomb monochromator. The relative radiation flux in quanta per second is shown in Figure 2. This is based on direct measurements of energy flux

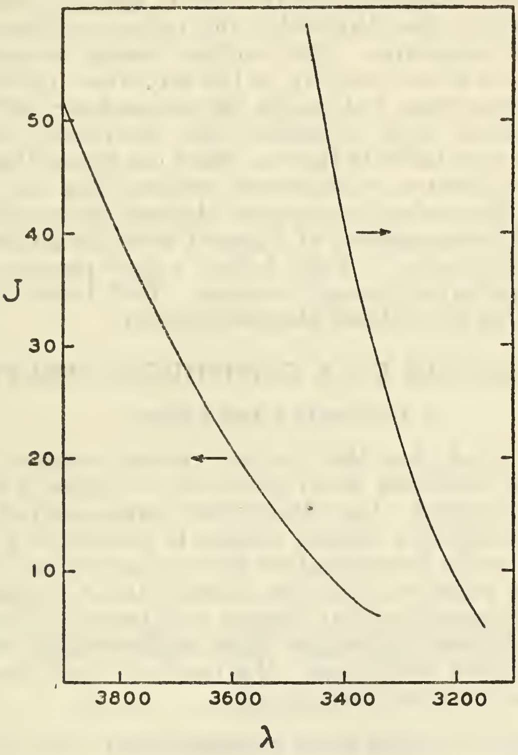


FIGURE 2.—*Relative values of radiation flux in quanta per second of light from a Mazda lamp resolved by a quartz monochromator*

made with a thermopile supplemented by computed values based on radiation laws, the dispersion of quartz and the transmission of glass from a similar lamp. The computed values were only used in the range 3,250 to 3,150.

## 3. PROPERTIES OF THE SPACE CHARGE TUBE

In a comparison of radiation, strongly absorbed in the front of the ionization chamber with radiation weakly absorbed throughout the length, it is important to know the sensitivity in different parts of the chamber. In a tube such as is shown in Figure 1 a small beam

of light was moved diametrically across the tube and no change in ionization greater than 10 per cent was found until the light beam struck the walls. Again in a tube of similar dimensions with a slit along the length of the cylinder no important change was found as the light was moved from one end of the cylinder to the other. The experiments do not exclude the existence of a thin layer of vapor (1 or 2 mm) at the window which is ineffective. Apart from this possibility we are justified in assuming that all ions produced in the chamber are equally effective.

There is a small surface effect which is greatest with the cæsium at room temperature. Then light of all wave lengths from the ultra-violet to the visible gives an increase in electron current with a sensitivity highest in the ultra-violet, but entirely different from the photo-ionization sensitivity. This current change increases as the thermionic current is increased up to the saturation value by raising the cathode temperature, but unlike the space-charge effect there is no further increase upon exceeding the saturation temperature. These and other tests indicate that the effect can be ascribed to photo-electric emission from a transparent caesium film on the quartz window.[9] The photo-electric emission changes the potential of the film which in the arrangement of Figure 1 acts like an external grid on the electron emission. With higher vapor pressures the film resistance and potential change decrease. Well below 100° C. the effect is masked by the volume photo-ionization.

## III. IONIZATION BY A CONTINUOUS SPECTRUM

### 1. INTENSITY RELATION

It has been found that the electron current change is not proportional to the ionization when the current change is comparable with the dark current.[10] For illumination with resolved light of a Mazda lamp the relative current change is commonly less than 10 per cent and a nearly linear relation between ionization and current change is to be expected. Mohler, Foote, and Chenault found a linear relation between current change and intensity for ionization by line absorption and the authors have confirmed this for a variety of wave lengths and conditions. We conclude that the ionization is directly proportional to the intensity.

### 2. EFFECT OF ELECTRON CURRENT AND VOLTAGE

Variation of the electron current by changing the filament temperature has no effect on the form of the sensitivity curve. Variation of the applied potential has the effect that strongly absorbed light, notably the 3,612 line, is slightly more effective at high voltage. This can be ascribed to the ability of higher electric fields to draw more ions from the layer of vapor close to the window. There remains no evidence that the ionization process depends on the electron current.

### 3. TEMPERATURE EFFECT

Careful tests were made to detect a change in the relative sensitivity when the cæsium pressure was kept constant and the tem-

[9] Ives, Astrophys. J., 62, p. 309; 1925.
[10] Whitman, B. S, Jour. Research, 4 (RP 138), pp. 157-167; January, 1930.

perature of the body of the tube was changed. Figure 3 illustrates the results at a cæsium pressure of 0.0038 mm and temperatures of 162° and 260° C. All results indicate that the relative height of the line peaks is independent of the temperature. Under the conditions of the experiment the pressure remained constant and the density changed. Following results indicate that maintaining a constant vapor density would probably not make a perceptible difference.

## 4. ABSORPTION EFFECT

It is evident from computations, such as those given in Table 1, that the absorption of a layer of vapor of several centimeters in

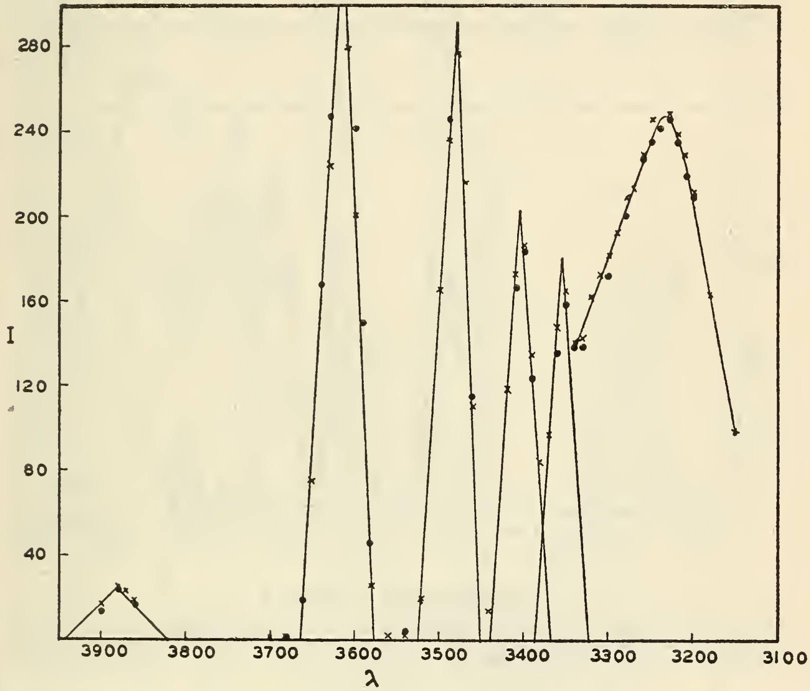


FIGURE 3.—*Ion current v. λ at 0.0038 mm*

Circles at 162° C. and crosses at 260° C.

front of the ionization chamber will appreciably reduce the light intensity at the center of the absorption lines even at pressures of $10^{-3}$ mm or less. Preliminary experiments made with a tube having the ionization chamber 8 cm from the window gave about one-fourth of the relative sensitivity at 3,612 A at a pressure of 0.001 mm which was obtained with the tube shown in Figure 1. The tubes used in previous investigations have had several centimeters of vapor in front of the ionization chamber so that the line absorption sensitivity was reduced.

Quantitative measurements of the absorption were made by placing a cell containing cæsium in front of the space-charge tube and making observations of the change in the ionization when the

cæsium in the absorption cell was heated. Figure 4 illustrates some curves obtained under extreme conditions with an absorption tube 30 cm long. Curves I and II show the observed curves with cæsium at a pressure of 0.14 mm in the space charge tube and at zero and 0.14 mm in the absorption cell. Curve III was obtained with the same pressure in the absorption cell but a much lower pressure, 0.0063 mm, in the space-charge tube. This indicates that there is complete absorption near the center of the lines at this pressure and that by lowering the pressure in the ionization chamber the lines become so narrow that no effective radiation is transmitted. It is interesting that the measurements for Curve II show no diminution in the small

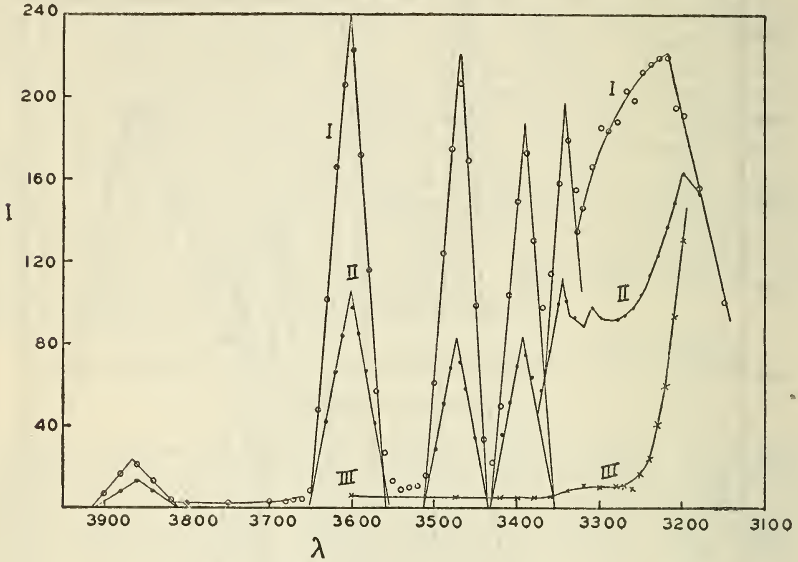


Figure 4.—*Ion current v.* λ

I with 0.14 mm of cæsium in the space charge tube; II with a 30 cm column of cæsium vapor at 0.15 mm pressure in the light path; III with the same absorbing column, but the pressure in the space charge tube reduced to 0.0063 mm.

effect between lines though this could not be shown on the scale of the drawing. This effect between the lines becomes much less at lower pressure.

More useful results were obtained at much lower pressures with an absorption cell 4 cm long. Table 2 summarizes the results and includes both the observed transmission $e^{-NLk}$ and $NLk$. A plot of $NLk$ versus wave length gives a nearly straight line and the values in the table are based on the best straight lines to smooth out accidental errors where $NLk$ is small. It is evident that $k$ is not a constant, but varies with the pressures in both the absorption cell and the space-charge tube. These variations are evidently a consequence of the shape of the absorption lines and the variation of their width with pressure.

TABLE 2.—*Absorption of radiation effective in producing ions by a 4 cm column of vapor*

| Wave length | Ionization chamber 0.0031 mm | | | | Ionization chamber 0.0059 mm | |
|---|---|---|---|---|---|---|
| | Absorption, 0.0011 mm | | Absorption, 0.0031 mm | | Absorption, 0.0031 mm | |
| | Transmission | *NLk* | Transmission | *NLk* | Transmission | *NLk* |
| 3,612 | 0.56 | 0.58 | 0.40 | 0.92 | 0.57 | 0.57 |
| 3,477 | .67 | .395 | .50 | .69 | .63 | .46 |
| 3,398 | .77 | .265 | .63 | .465 | .73 | .31 |
| 3,347 | .83 | .185 | .72 | .33 | .80 | .22 |
| 3,300 | .90 | .105 | .83 | .19 | .88 | .125 |
| 3,250 | .978 | .022 | .955 | .045 | .965 | .035 |
| 3,200 | 1.0 | 0 | 1.0 | 0 | 1.0 | 0 |

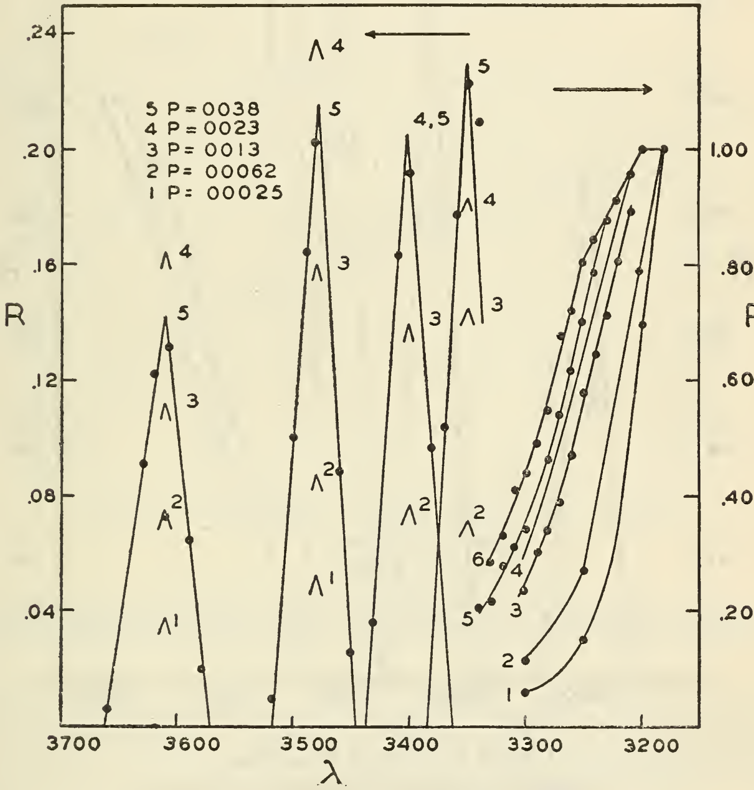


FIGURE 5.—*Relative sensitivity v.* λ

1 at 0.00025 mm, 2 at 0.00062 mm, 3 at 0.0013 mm, 4 at 0.0023 mm, 5 at 0.0038 mm, 6 at 0.0073 mm. Two scales of *R* left for 3,700 to 3,340, right 3,340 to limit.

## 5. PRESSURE EFFECT

It is feasible to investigate an extreme range of pressures, and Figures 5 and 6 show the relative sensitivity, *R*, as defined in equation (3) for pressures ranging between $2.5\times10^{-4}$ and 0.15 mm. At each wave length *R* rises and then falls with increasing pressure in a

manner which suggests that there are two or more effects which nearly counterbalance each other above 0.002 mm pressure. Ordinates give the effect relative to the limit and since the ionization at the limit is proportional to the pressure the ionization at all wave lengths is always increasing with pressure throughout the range studied.

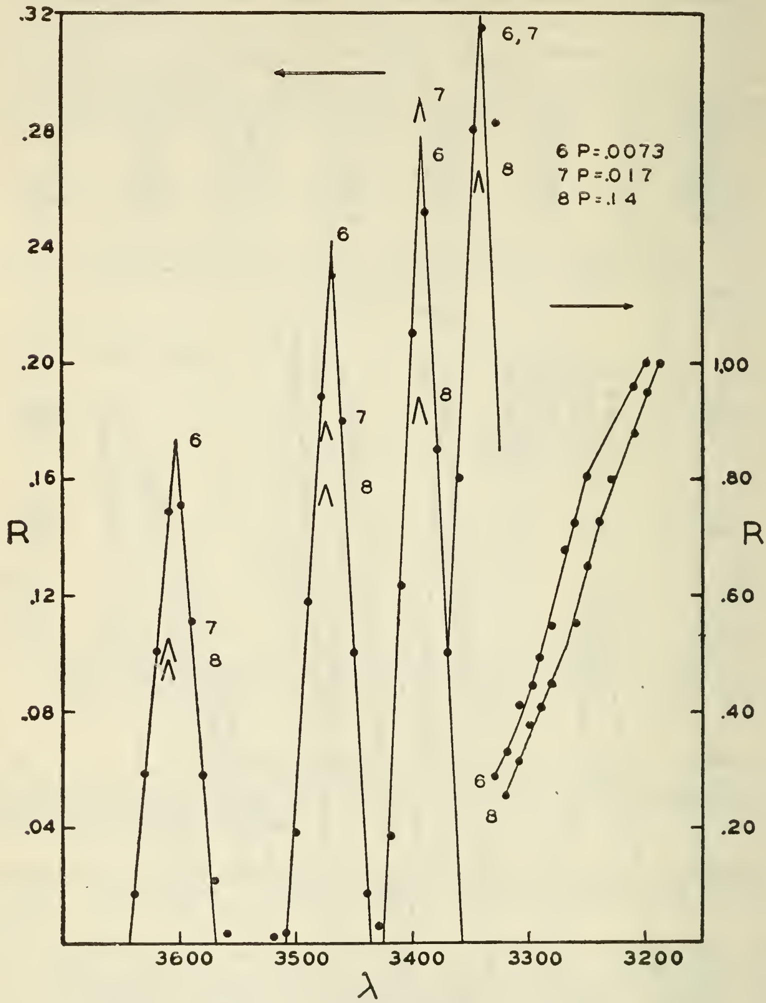


FIGURE 6.—*Relative sensitivity v.* λ

6 at 0.0073 mm, 7 at 0.017 mm, 8 at 0.14 mm. Two scales of *R*.

## 6. QUENCHING BY FOREIGN GASES

It is difficult to maintain a good vacuum in a sealed-off tube containing an alkali metal, so a preliminary experiment was made with the tube connected to the pumps through a capillary which could be closed with a needle valve. The relative sensitivity to line absorption gradually increased with prolonged pumping to a value appreciably higher than previously obtained in sealed tubes. The experi-

ments furnished a standard for estimating the vacuum in sealed-off tubes, and in the results quoted in this paper the quenching by foreign gas is probably negligible. Quantitative measurements of the effect of adding foreign gases will be presented in another paper.

## IV. IONIZATION BY HELIUM LINES

### 1. THE HELIUM LINE AT 3,888 A

The helium spectrum contains an isolated strong line at 3,888.649 A while the red component of the third doublet of cæsium is at 3,888.622 A. This is very nearly exact coincidence and it was expected that this line would be strongly absorbed by cæsium and give a large photo-electric effect. Experiments bore out this expectation and it

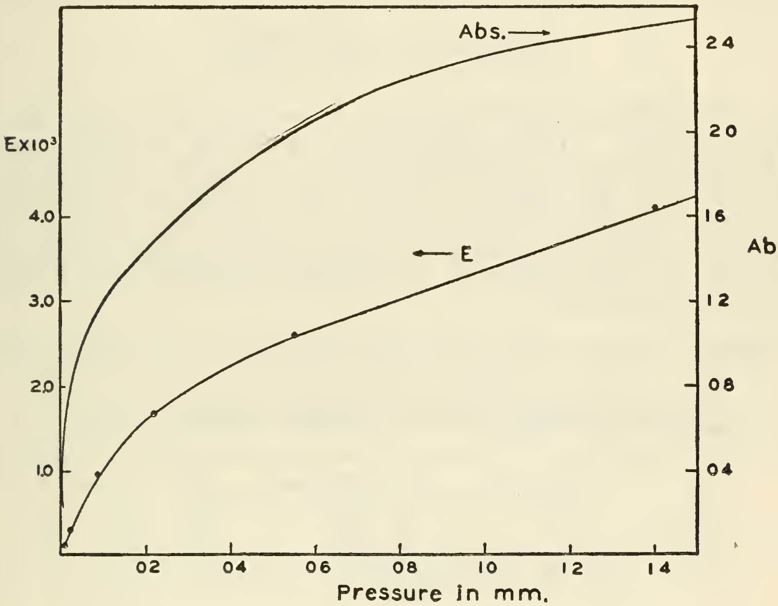


FIGURE 7

Upper curve, right scale, the absorption of the 3,888 helium line by a 4 cm column of cæsium vapor as a function of cæsium pressure. Lower curve, left scale, the quantum efficiency of ionization of cæsium by 3,888 as a function of pressure.

was possible to make direct measurements of the radiation flux, the fraction of this radiation absorbed, and the number of ions produced. Such measurements in contrast to studies with continuous radiation yield directly the probability of ionization of an excited atom (or the quantum efficiency of ion production) without assumptions as to line width and shape.

A small capillary Geisler tube served as a source and the radiation flux for 3,888 and for the 3,130 line of mercury were measured directly by a thermopile under operating conditions. The former was barely measurable so that the absolute value of the final result is much less certain than the relative values.

Absorption of the 3,888 line was measured with a 4 cm absorption cell and a photo-electric cell, and Figure 7, upper curve, shows the absorption as a function of the pressure.

Photo-ionization was measured by a direct comparison of the ionization produced by 3,888 and the 3,130 line of the mercury arc. The effect of both lines was so large that the current change was not proportional to the ionization and it was necessary to determine the current intensity relation at each pressure by reducing the light in known ratios by a series of wire gauze screens. The relative sensitivity $R$ is then

$$R=\frac{I\ (3{,}888)}{I\ (3{,}130)}\times\frac{J\ (3{,}130)}{J\ (3{,}888)}$$

where the $I$'s are the corrected ratio of ionization and the $J$'s are the radiation flux in quanta per second. Assuming that the quantum efficiency of the 3,130 radiation is one, we have for the efficiency of 3,888;

$$E\ (3{,}888)=R\times\frac{Abs\ (3{,}130)}{Abs\ (3{,}888)}$$

The absorption of 3,130 has been determined by the authors as $NL\times 1.85\times 10^{-19}$. Table 3 summarizes the data for the determination of $E$ and Figure 7, lower curve, is a plot of the results. It is seen from the table that the relative sensitivity rises and falls with increasing pressure in the same general manner as $R$ for the effect of continuous radiation. The ratio remains of the order of one because the low efficiency is counterbalanced by the high absorption of 3,888 as compared with 3,130.

TABLE 3.—*The absorption and ionization of cæsium by the 3,888 helium line*

| Cæsium temperature (°C.) | Cæsium pressure | $R$ (3,888) | Absorption of 3,130 | Absorption of 3,888 | $E$ (3,888) |
|---|---|---|---|---|---|
| 110 | $0.64\times10^{-3}$ | 0.42 | $0.096\times10^{-4}$ | 0.036 | $0.11\times10^{-3}$ |
| 128 | 1.9 | .77 | .285 | .078 | .28 |
| 156 | 8.5 | .89 | 1.28 | .118 | .96 |
| 173 | 22 | .75 | 3.3 | .150 | 1.65 |
| 193 | 55 | .63 | 8.3 | .20 | 2.6 |
| 214 | 140 | .49 | 21 | .25 | 4.1 |

## 2. IONIZATION BY 3,188 A OF HELIUM

Another helium line which gives measurable photo-ionization is at 3,187.743 $A$. This is within 4 Angstroms of the cæsium series limit. We compute from the series formula given by Miss Mathews [11] that the forty-eighth line lies at 3,187.73, the forty-ninth at 3,187.55. Experiments were limited to a direct comparison of the effect of this line and 3,130 of mercury. For pressures ranging from 0.001 to 0.07 mm there was no change in the relative sensitivity.

## 3. IONIZATION BY OTHER LINE SOURCES

Strong emission lines, such as 3,650 and 3,340 of mercury which are many Angstroms from cæsium absorption lines, give measurable photo-ionization. This is evidently related to the small effect between lines observed with a continuous spectrum at the higher pressures. Results of experiments on this effect will be published later.

[11] Mathews, Proc. Roy. Soc., **120**, p. 650; 1928.

## V. DISCUSSION

### 1. RESTRICTION OF THE PROBLEM

Ionization by line absorption involves initially the production of an excited atom in an $m\ P$ state. The energy of this state is appreciably below the ionization potential, 0.7 volt below in the extreme case of ionization by the 3,888 line. What is the source of the additional energy required for ionization? The experiments definitely eliminate most of the possibilities. The linear relation between intensity and ionization rules out the hypothesis of a transfer of energy between two excited states. The evidence that sensitivity is independent of electron current shows that ionization is not produced by electron collisions. The absence of temperature effect eliminates the theory that ionization results either directly or indirectly from thermal agitation or from black body radiation. There remains the possibility suggested by Franck that an excited atom in collision with a normal atom forms a molecule which spontaneously becomes ionized. This theory seems to be strongly supported by the experiments though it involves too many unknowns to be definitely established. The probability of ionization would depend on the pressure in a complicated manner. The chance of absorption of a quantum of radiation and the chance that the exicted atom collides to form a molecule before radiation takes place will vary with pressure and possibly the chance of subsequent ionization may depend on pressure as well. The measurements on the ionization by the 3,888 helium line give directly the efficiency of ionization per quantum absorbed. In the following section we attempt to derive this quantum efficiency for ionization at the other lines and thus eliminate the first cause of pressure variation. It remains then to see if the variation in quantum efficiency with pressure can be accounted for by the second pressure effect.

### 2. CORRECTION FOR ABSORPTION

If $I(\nu)$ is the number of ions produced per second by a flux of $J(\nu)\,\Delta\nu$ quanta per second in a band of width $\Delta\nu$, then

$$I(\nu) = \int_{\Delta\nu} E(\nu)\, J(\nu)\,(1 - e^{-NLk})\, d\nu \tag{5}$$

where $E(\nu)$ is the quantum efficiency. Assuming that absorption in a line can be expressed as a constant absorption $k_m$ over a width $\delta\nu$, then

$$I(\nu) = E(\nu)\, J(\nu)\,(1 - e^{-NLk_m})\,\delta\nu \tag{6}$$

At the series limit $E = 1$ and since $NLk_o$ is very small $1 - e^{-NLk_o} = NLk_o$ and

$$I_o = J_o NLk_o \Delta\nu \tag{7}$$

$$E(\nu) = \frac{I(\nu)}{I_o}\ \frac{J_o NLk_o\,\Delta\nu}{J(\nu)\,(1 - e^{-NLk_m})\,\delta\nu}$$

$$E(\nu) = R(\nu)\ \frac{NLk_o}{1 - e^{-NLk_m}}\,\frac{\Delta\nu}{\delta\nu} \tag{8}$$

where $R(\nu)$ is the quantity plotted in Figures 5 and 6. Where lines are unresolved (3,300 to 3,200) we can make use of the law of absorption near the limit

$$\int_{\Delta\nu} NLkd\nu = NLk_o\Delta\nu$$

If $Nlk_m$ is sufficiently small (less than 0.2) so that $1-e^{-NLk}=NLk$, we have the simple relation that $E(\nu)=R(\nu)$. When $NLk_m$ is larger, then $E$ is greater than $R$ and we can use the approximation

$$E(\nu)=\frac{R(\nu)\,NLk_m}{1-e^{-NLk_m}} \tag{9}$$

where $k_m$ applies to one of the unresolved lines near the center of the slit.

In column 5 of Table 2 we have given the measured value of $NLk$ for 4 cm of cæsium vapor at 0.0031 mm for radiation effective in producing ionization at the same pressure. From column 5 of Table 1 we can compute $\int NLkd\nu = NLk_m\delta\nu$ for the same condition, and the quotient gives a value of $\delta\nu$ that can be used in equation (8) for the effective width of our assumed rectangular line at this pressure. Table 4 gives the results and we will use the mean value $\delta\nu=0.065$ cm$^{-1}$ or $\delta\lambda=0.0076$ A. This value is if anything too small, for the Doppler width is 0.0055 A and taking into account the fine structure we would expect an effective width of about 0.01 A. It is important to note that Waibel's values of $\int kd\nu$ would give $\delta\lambda$ only a fifth as large as this, which is clearly impossible.

Table 4.—*The effective line width for absorption at 0.0031 mm*

| Wave length | $NLk\,\delta\nu$ from Table 1 | $NLk$ from Table 2 | $\delta\nu$ | $\delta\lambda$ |
|---|---|---|---|---|
| 3,250 | $0.6\times10^{-2}$ | 0.045 | 0.13 | 0.0140 |
| 3,300 | 1.34 | .190 | .071 | .0077 |
| 3,349 | 1.97 | .33 | .060 | .0067 |
| 3,398 | 2.50 | .46 | .054 | .0062 |
| 3,477 | 4.2 | .69 | .061 | .0074 |
| 3,612 | 7.2 | .92 | .078 | .010 |

Table 5.—*Quantum efficiency at 0.0038 mm*

| Wave length | $NLk\,\delta\nu$ from Table 1 | $NLk$ for $\delta\nu=0.065$ | $R$ from Figure 5 | Correction equations (8) and (9) | $E$ |
|---|---|---|---|---|---|
| 3,200 | | | 1.00 | 1.0 | 1.00 |
| 3,225 | | | .90 | 1.0 | .95 |
| 3,250 | $7.3\times10^{-3}$ | 0.11 | .72 | 1.05 | .76 |
| 3,300 | 19 | .29 | .34 | 1.15 | .39 |
| 3,349 | 24 | .37 | .23 | 1.05 | .24 |
| 3,398 | 30 | .47 | .20 | .87 | .18 |
| 3,477 | 51 | .79 | .214 | .59 | .126 |
| 3,612 | 87 | 1.35 | .14 | .44 | .062 |
| 3,888 | 168 | 2.6 | .0043 | .35 | .0015 |

TABLE 6.—*Quantum efficiency as a function of pressure*

| Wave length | Pressure | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.00025 | 0.00062 | 0.0013 | 0.0023 | 0.0038 | 0.0073 | 0.017 | 0.14 |
| | $\delta\nu$ | | | | | | | |
| | 0.065 | 0.065 | 0.065 | 0.065 | 0.065 | 0.09 | 0.137 | 0.395 |
| 3,200 | 0.75 | 0.80 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 3,225 | .47 | .55 | .76 | .84 | .90 | .93 | .90 | .93 |
| 3,250 | .15 | .28 | .57 | .67 | .76 | .86 | .80 | .89 |
| 3,300 | .06 | .12 | .25 | .32 | .39 | .52 | .58 | .74 |
| 3,347 | ---------- | .066 | .14 | .18 | .24 | .35 | .39 | .57 |
| 3,398 | ---------- | .056 | .10 | .166 | .18 | .26 | .31 | .39 |
| 3,477 | .02 | .038 | .074 | .124 | .126 | .16 | .15 | .31 |
| 3,612 | .009 | .020 | .033 | .059 | .062 | .092 | .075 | .19 |
| 3,877 | ---------- | .0005 | .001 | .0011 | .0015 | .002 | .0023 | .0067 |

To compute the quantum efficiency $E$ from $R$ by equations (8) and (9) we will make the arbitrary assumption that $\delta\nu = 0.065$ for

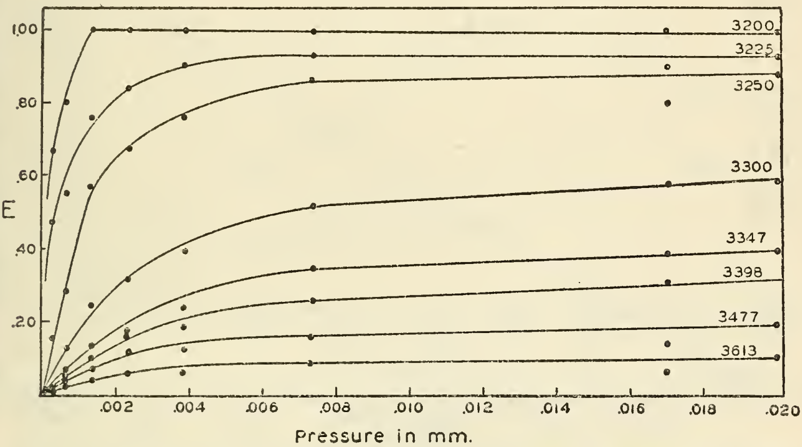


FIGURE 8.—*Quantum efficiency of radiation of various wave lengths for producing ionization as a function of cæsium pressure from data of Figures 5 and 6*

all pressures less than 0.0038 mm and that for higher pressures $\delta\nu = 0.065\sqrt{\frac{p}{0.0038}}$. This relation is consistent with Waibel's width measurements at high pressures. Fortunately corrections are relatively small for the lower pressures, but with increasing pressure the results become increasingly uncertain. Table 5 shows the data for the computation of the quantum efficiency $E$ for one pressure; while Table 6 and Figure 8 summarize results at eight pressures. The correction term for resolved lines based on equation (8) involves the ratio of the integral of the continuous absorption across the slit to the integral of the line absorption across the line and this important part of the correction is independent of the arbitrary assumption as to line width. A mean value of the width $\Delta\nu = 303$ cm$^{-1}$ has been used. The tables include values of $E$ for 3,877 and 3,888 based on the same series

of measurements, but not included in Figures 5 and 6. The values are about twice as great as obtained for 3,888 ionized by the helium line but the difference can be accounted for both in the large error in the absolute value of the latter and in the failure of the above approximations where absorption is high. Figure 8 shows a regular progression of $E$ with the series term and with the pressure that was not apparent in the original data on relative sensitivity. The constant value of $E$ for a setting at 3,200 $A$ for pressures above 0.001 mm is confirmed by the constant relative sensitivity to the 3,188 line of helium and in the latter case there is no question of insufficient resolution masking a change. Other wave lengths except 3,877 and 3,888 seem also to approach a constant but lower efficiency at higher pressures.

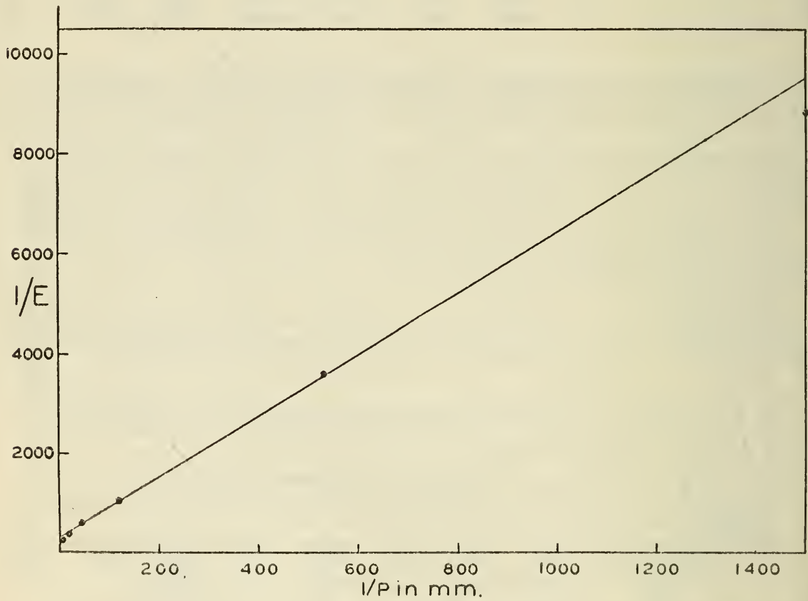


FIGURE 9.—*Plot of reciprocals of quantum efficiency and of pressure for 3,888 from data of Figure 7*

### 3. THE PRESSURE VARIATION OF EFFICIENCY

Franck's theory of ionization by molecule formation requires that the excited atoms collide during the life of the excited states. The probability $P$ of this will depend on the pressure according to the equation [12]

$$P = \frac{\tau}{T + \tau} = \frac{1}{1 + 1/A\sigma^2\tau p} \tag{10}$$

where $\tau$ is the mean life of the excited state and $T$ is the average time between collisions between excited atoms and normal atoms. $T = 1/p\sigma^2 A$ where $\sigma$ is the distance between atom centers at collision, $p$ is the pressure in mm and $A = 2.45 \times 10^{21}$ for cæsium atoms at 500° K.

[12] Turner, Phys. Rev., 23, p. 464; 1924

We will assume that the probability of ionization after a collision, $E_c$ is independent of pressure and see if the relation $E=P\ E_c$ accounts for the pressure variation of $E$. From equation (10)

$$E=E_c\frac{1}{1+1/A\sigma^2\tau p}$$

$$\frac{1}{E}=\frac{1}{E_c}\left(1+\frac{1}{A\sigma^2\tau p}\right) \tag{11}$$

A plot of the reciprocals of $E$ and $p$ should give a straight line with the intercept on the $1/p$ axis equal to $1/E_c$ and the slope equal to this

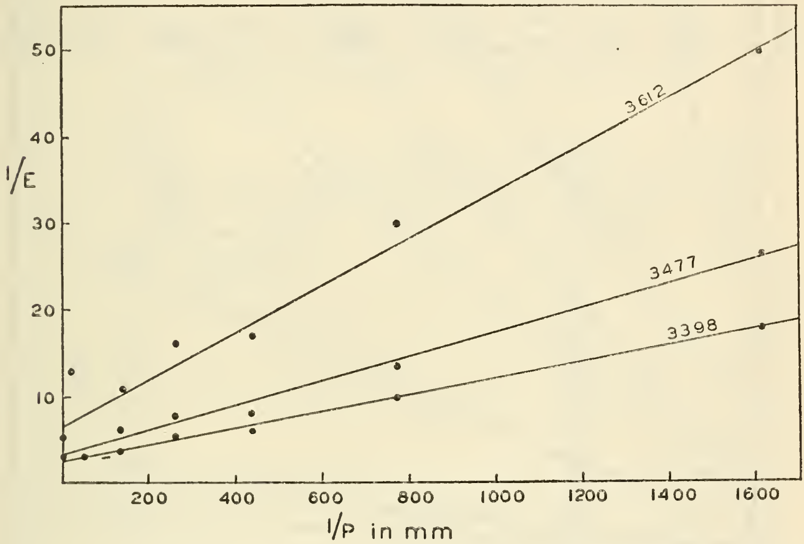


Figure 10.—*Reciprocal plots of quantum efficiency and pressure from data of Figure 8*

times $1/A\sigma^2\tau$. Figure 9 shows such a plot for the data on quantum efficiency of ionization by the 3,888 helium line. Here the small deviation near the origin on the reciprocal scale represents a rather large departure from the linear relation at high pressure where experimental error is small. Figures 10 and 11 give reciprocal plots of the quantum efficiency computed from the data on ionization by a continuous spectrum. Here the accidental error is much greater and the straight lines give as close an approximation as could be desired. There are many factors which could give a deviation such as observed in the curve of Figure 9, notably imprisonment of resonance radiation or any other feeding back of energy following the first collision. We conclude that the pressure variation of quantum efficiency is largely accounted for by the variation in the chance of a collision during the life of an excited state and that the probability of ionization at a collision is apparently independent of pressure as well as temperature.

Table 7 gives the numerical values of $E_c$ and $\sigma^2\tau$ computed from the reciprocal plots. Unfortunately there is no safe basis for estimat-

ing either $\sigma^2$ or $\tau$ independently. The values of the products are surprisingly large. From $\int k d\nu$ one computes a life which measures the average time between absorption and emission of the absorbed line and this is certainly longer than the actual life until any line is emitted. For 3,612 it is $1.2 \times 10^{-5}$ seconds. There are nine other permitted transmissions from 5 $P_2$ to $mS$ and $mD_{23}$ and with the crude approximation that all are equally possible the life would be about $10^{-6}$ seconds. Thus it is seen that the distance of approach for an effective collision with an atom in the 5 $P$ state is probably between

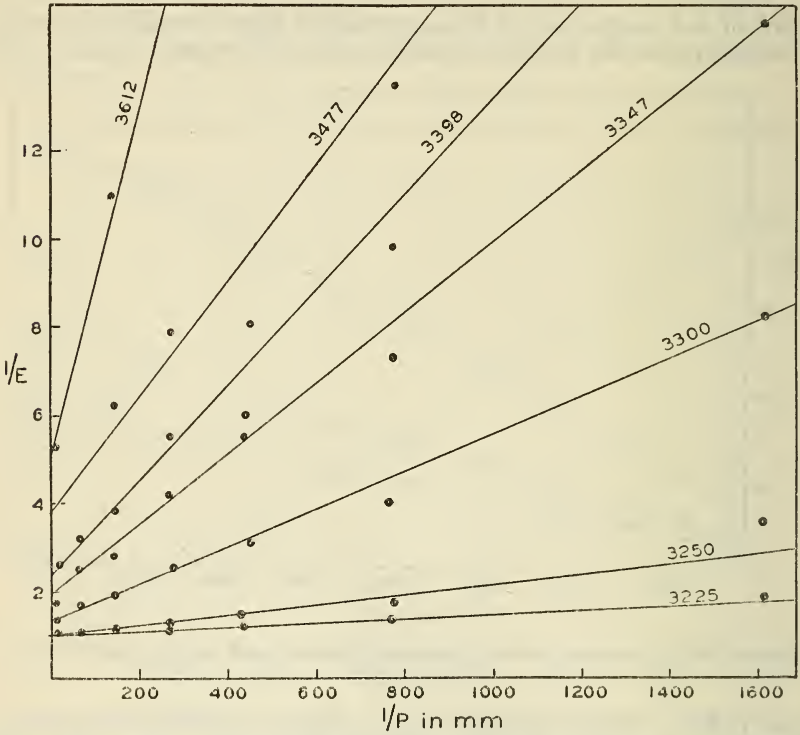


Figure 11.—*Reciprocal plots of quantum efficiency and pressure from data of Figure 8*

$10^{-7}$ and $3 \times 10^{-7}$ cm which is very large even for the greatest possible life. For states 6 $P$ to 10 $P$ the life would progressively increase on the above viewpoint so that $\sigma^2$ must decrease to keep the quantity $\sigma^2\tau$ nearly constant. Apparently the large effective radius is not related in a simple manner to the radius of distribution of charge in the $mP$ state which is continuously increasing with $m$. These details are highly speculative, but the general conclusion as to the magnitude of the product rests directly on the observations of relatively large effects at very low pressure regardless of assumptions as to absorption corrections or the exact nature of the pressure variation of $E$.

TABLE 7.—*Constants derived from Figures 9, 10, and 11*

| $m$ | $1S-mP$ | $E_c$ | $\sigma^2\tau$ |
|---|---|---|---|
| 4 | 3,888 | 0.003 | $0.22\times10^{-19}$ |
| 5 | 3,612 | .154 | $1.0\times10^{-19}$ |
| 6 | 3,477 | .26 | $1.1\times10^{-19}$ |
| 7 | 3,398 | .40 | $1.1\times10^{-19}$ |
| 8 | 3,347 | .50 | $1.0\times10^{-19}$ |
| 9, 10 | 3,300 | .77 | $1.2\times10^{-19}$ |
| 12, 13 | 3,250 | .89 | $3.3\times10^{-19}$ |
| 16 | 3,225 | .93 | $16\times10^{-19}$ |
| 25 | 3,200 | 1.00 | $48\times10^{-19}$ |

## 4. THE HYPOTHESIS OF MOLECULE ION FORMATION

The results are consistent with Franck's theory that excited atoms when they collide with normal cæsium atoms form molecule ions.

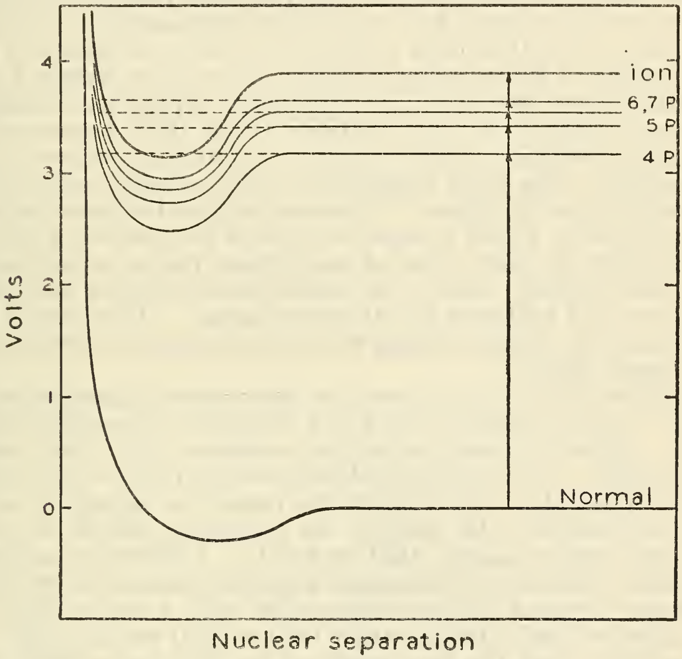


FIGURE 12.—*A Franck Condon diagram of potential energy v. nuclear separation to illustrate the process of molecular ion formation by atomic line absorption*

The ionization potential of the atom is 3.87 volts and the longest wave length which produces ions is 3,888 corresponding to 3.17 volts. We conclude that the potential energy of the molecule ion is at least 0.70 volt less than that of an atom and an atom ion; that is, the work of dissociation of the molecule ion is greater than 0.70 volt. As the probability of ionization by 3,888 is very low, probably this value is close to the threshold and $D^+$ is nearly 0.7 volt. The energy relations are represented in Figure 12 in the form of a Franck Condon diagram. We have used the convention that the origin of ordinates is the energy of 2 normal atoms; hence, the energy of a normal molecule is

negative. With this convention the ordinates for large values of the atomic separation give the atomic energy levels. The only important detail is that the minimum for the normal ion is at least as low as shown. The process of molecule formation is then, first, the excitation process raising the atomic energy along a vertical line at the right; second, the collision process is a motion to the left nearly coincident with one of the horizontal lines (kinetic energy of thermal agitation is barely perceptible on this scale); third, the recombination process involves a slight dissipation of energy along this horizontal path so that the broken line portion of the path is a quantized state of the excited molecule. Then the atom will oscillate back and forth along this portion of the line until a transition occurs; fourth, the transition will occur either to the ion state or to some lower molecule state.

The chance that it goes to the ion state will depend on the area between the horizontal line and the potential energy curve for the ion in an unknown way, but will clearly increase as we go to higher series terms. We thus have a reason why the probability of ionization at collision, $E_c$, increases regularly as we go to higher $P$ states. The experimental fact that this probability approaches certainty for high states shows that the probability of the third process—that of combination—is also almost certainty for high states and possibly for all states. The large magnitude of the collision radius can also be visualized from this figure. If we assume that the potential minima have abscissae of about 2 Angstroms, as is the case for a potassium molecule, then the least value of the collision radius would fall at the edge of the drawing; that is, an excited atom reaching any point on the figure would be drawn into the other atom. The potential energy curves must be slightly sloping and not horizontal as drawn over the entire length shown.

The value of 0.7 volt or more for the work of dissociation of the molecule ion indicates that it has a stability comparable with $Na_2$ and $K_2$. There is some supporting evidence that alkali molecule ions are stable. Ives [13] gives evidence that the positive ions produced by a hot filament in alkali vapors are molecular aggregates at a low vapor temperature. In cæsium the molecular weight is 1,000 at 0° C., but nearly atomic (133) at 60° C. Ditchburn and Arnot [14] have shown that atomic potassium ions shot through a jet of potassium vapor become diatomic molecules with a probability nearly independent of their kinetic energy between 200 and 20 volts. They find, however, that the ions produced by the photo-electric ionization of potassium by an iron arc are purely atomic.

If in cæsium vapor the continuous absorption gives atomic ions and the line absorption gives molecules, the question arises as to whether the space-charge method gives directly the ratio of ions as we have assumed. In view of the fact that ions take a long time to produce their space-charge effect, it is probable that an equilibrium ratio of molecule and atom ions is reached which is quite independent of their initial state.

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[13] Ives, J. Frank. Inst., 201, p. 47; 1926.
[14] Ditchburn and Arnot, Proc. Roy. Soc., 123, p. 516; 1929.

## VI. SUMMARY

The results show that the ionization of cæsium vapor by light on the red side of the limit is the result of line absorption (neglecting a small effect between lines) in lines of a width of the order of 0.01 *A* or less below 0.01 mm pressure.

The subsequent ionization is independent of temperature and electrical conditions but depends on the vapor pressure in a manner which suggests that a collision with a normal cæsium atom must occur during the life of the excited state. The chance of ionization at a collision increases from a very low value for the 4 *P* state to nearly one for 16 *P*. The collision distance depends on the life of the excited state which is unknown, but this distance is certainly large compared with usual atomic dimensions.

WASHINGTON, January 4, 1930.